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ELECTRODEPOSITION OF ALLOYS

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I. INTRODUCTION. PHYSICOCHEMICAL PROPERTIES AND APPLICATIONS OF ELECTRODEPOSITED ALLOYS

The evolution of modern technology makes increased demands on the physicochemical properties of metallic surfaces. In several cases they must possess definite properties (corrosion resistance, magnetic properties, high dielectric constant, etc.), and quite often even a combination of such properties. Surfaces having specified properties can be produced by depositing alloys consisting of two or more metals.

The electrodeposition of alloys under conditions of simultaneous discharge of the ions has attracted considerable interest during recent years†. The resulting alloys have wide and varied uses in technology. For example, zinc–cadmium alloys[1] are distinguished by high corrosion resistance in tropical climates, and lead–tin alloys in seawater; alloys based on chromium show improved retention of mechanical properties at high temperatures and are very resistant to oxidation[2-4]; cobalt–nickel alloys have high chemical resistance and hardness, silver–cadmium alloys a high optical reflectivity which does not change with time, and alloys of lead with copper or silver good antifriction properties. Finally, a deposit which has long been known — brass — has recently acquired wide use as a preliminary coating of steel before nickel or chromium plating, and also in the manufacture of shock-absorbers, as an intermediate layer in the application of rubber to steel[5].

Furthermore, under conditions of the codeposition of metals it becomes possible to deposit in an alloy even metals which cannot be obtained in pure form from aqueous solution. It also becomes possible to deposit alloys based on metals of high melting point, for example tungsten[6-17], molybdenum[18-25], and rhenium[26,27]. Such coatings of heat-resistant alloys possess several engineering and economic advantages.

The above properties of electrodeposited alloys, as well as their finely crystalline structure, density, increased hardness, and other properties, have been responsible for their ever extending application in industry. At the present time practical electroplating has been undertaken with alloys based on copper[5,28-33], lead[34-42], nickel[43-47], tin[48-64], and other metals. Methods for electrodepositing alloys of three or four metals have also been developed[14,65-76].

The number of papers published on the electrodeposition of alloys has also increased considerably during recent years. However, most of them deal with applied problems in the development of a formula and the technical conditions for the production of a given alloy. Comparatively few consider questions of the structure of the alloys, the conditions for their electrodeposition, and the kinetics of electrode processes involving the codeposition of metals.

Study of the electrodeposition of one metal is linked with the solution of many individual problems. The complexity of processes involved in the formation and growth of metal crystals by the discharge of ions is responsible for the variety of methods used in their investigation.

In the electrodeposition of alloys, additional difficulties appear, as a result of the simultaneous discharge of two or more types of ions, connected both with the change in activity of the reducible ions in the layer adjacent to the cathode and with the change in nature and state of the cathode surface. In order to ascertain the conditions for the production of alloys, therefore, investigation of the kinetics of electrode processes must be accompanied by a study of the properties of the electrodeposits.

II. STRUCTURE OF ELECTRODEPOSITED ALLOYS

Alloy deposits formed by the simultaneous deposition of metals on a cathode differ considerably in properties from alloys obtained by a thermal method. Electrodeposited alloys are harder, non-homogeneous, and finely crystalline. Considerable interest therefore attaches to investigating the structure of electrodeposited alloys and to ascertaining the extent to which their phase constitution corresponds to the equilibrium diagram. Establishment of the relation between the conditions of crystallisation of the alloys and their properties is also extremely important.

The structure of alloys is usually investigated with X-rays[38,57,77-85]. In several cases alloys obtained by electrodeposition and by the thermal method have identical structure[28,86-92].

The literature also contains references to the ability of electrodeposited alloys to form supersaturated solid solutions. Thus an increased proportion of one component has been observed in alloys whose components are mutually insoluble at low temperatures (for example Cu–Pb[81] and Ag–Pb[38]) and in several other alloys (Pb–Sn[57], Cu–Sn[80], Ag–Tl[91], and Ag–Bi[92]). On the other hand, an alloy belonging to a eutectic type of system (Cd–Zn) consists of a mixture of crystals of each component[93].

Considerable differences in the structure of the same alloys have been observed when they are obtained under different conditions. Depending on the conditions of deposition, Cd–Ag alloys contain solid solutions in some cases[87,89] and three phases (α, β, and γ) in other cases[94], these phases differing in composition from the corresponding phases in cast alloys. Thus electrodeposited alloys quite often differ appreciably in physical and mechanical properties from cast alloys, and are characterised by distortions of the crystal lattice. The phase constitution of such alloys depends on the conditions under which they have been electrodeposited.

From an investigation of the structures of a large number of alloys, Raub[82] concluded that, in the crystallisation of electrodeposited alloys, solid solutions can be formed only when codeposition of the metals already occurs at the lowest current densities. In such a case, the electrodeposited alloys do not differ in structure from cast alloys

† The production of alloys by electrodepositing one metal on a foreign cathode, which is then heat-treated, has not been widely used.

of corresponding composition. If, however, discharge of ions of one of the components begins only when a definite current density has been reached, the alloy consists of a mixture of the components.

The X-ray method does not always yield sufficiently complete information on the structure of electrodeposited alloys. In several cases the X-ray patterns contain diffuse lines, and only a proportion of the phases present in alloys can be determined. As a result, it has become necessary to use indirect methods as well. Combination of data from X-ray and thermographic investigations, density, magnetic properties, and superconductivity at low temperatures makes it possible to determine the phase structure of alloy electrodeposits[95-99]. By the above methods, for example, copper–bismuth alloys deposited at various potentials have been shown to contain a mixture of copper and bismuth crystals (in conformity with the phase diagram), a supersaturated solid solution phase, and a metastable phase of chemical compound type[100].

Gorbunova and Polukarov[101] have examined the mechanism of alloy formation and the dependence of phase structure on electrochemical conditions of deposition for systems characterised by different types of interaction between the components; this represents an extremely promising line of research.

The concepts associated with the formation and growth of a new phase have been enlisted to solve the problem of the mechanism of alloy formation on the cathode. Additional energy is required[102-105] for the formation of a crystal nucleus of a new phase on a foreign metal, and in the case of electrolysis this is represented by an increase in potential immediately after the current has been switched on.

Under the conditions of cathodic alloy deposition, the production of supersaturated solid solutions will obviously be determined to a considerable extent by the difficulty of forming a new phase of the metal which is the more electronegative in the given solution. Here two possible cases are distinguished[101]: (1) the potential of steady deposition is more positive than the potential required for formation of a crystal nucleus of the more electronegative metal, but exceeds its equilibrium potential; (2) the potential of steady deposition of the metal exceeds the potential of nucleus formation. In the former case a homogeneous system — a (supersaturated) solid solution — can be formed. In the latter case, however, the cathodic deposit will consist of a mixture of the components: *i.e.* formation of two-phase systems is possible. If the differences in atomic radius are considerable, inclusion of a second component in the lattice of the more positive metal may result in distortion of the lattice, which in turn requires the consumption of additional energy.

With increase in cathodic overpotential, the energy states of the reduced atoms of the more electropositive metal also change; this produces increased solubility of the second component in this metal with the formation of a supersaturated solid solution phase. Thus the magnitude of the cathodic overpotential has an important effect on the phase constitution of electrodeposited alloys. Therefore alloys containing every possible kind of phase can be formed in the simultaneous electrodeposition of metals on a cathode, independently of the form of the phase diagram. Deposition of the components of an alloy at high overpotentials may result in the formation on the cathode of phases which are not found in the usual equilibrium systems.

The formation of metastable phases, in particular, is of practical interest for the production of magnetically rigid materials of high coercivity. The appearance of such properties in alloys is governed by the size and shape of the crystals of the ferromagnetic phase and by the internal stresses at the interface between solid solution and chemical compound. Among such alloys can be included Co–Ni[106-109] and Co–W[100] electrodeposits, which are applied as coatings in the memory devices of electronic computers and in sound-recording apparatus.

However, the limiting solubility of the components is determined not only by the cathodic overpotential but also by the kinetics of the deposition process, and can therefore be affected by other conditions of electrolysis.

The question of the phase structure of electrodeposited alloys and its dependence on electrochemical conditions of deposition is of considerable interest for the practice and theory of the electrodeposition of alloys, but a more detailed consideration of this topic is beyond the scope of the present review.

III. THERMODYNAMIC CONDITIONS FOR SIMULTANEOUS ELECTRODEPOSITION OF METALS

The possibility of the simultaneous electrodeposition of metals with formation of an alloy on the cathode is governed by definite thermodynamic and electrochemical conditions.

In the case of two metals M_1 and M_2, codeposition can occur when their deposition potentials become equal. Each potential φ can be represented as the sum of two components — the reversible or equilibrium potential φ_{eq} and the polarisation η, which represents the irreversible consumption of energy required to maintain the process at a definite rate:

$$\varphi = \varphi_{eq} - \eta. \quad (1)$$

The equilibrium potential of a given metal depends both on the activity of the ions undergoing discharge $a_{M^{n+}}$ and on the activity of the metal on the electrode a_M:

$$\varphi_{eq} = \varphi_0 + \frac{RT}{nF} \ln \frac{a_{M^{n+}}}{a_M}, \quad (2)$$

where φ_0 is the standard electrode potential of the metal. For the deposition of a pure metal on a cathode of the same metal, where the activity of the metal is taken as unity ($a_M = 1$), Eqn. (2) becomes

$$\varphi_{eq} = \varphi_0 + \frac{RT}{nF} \ln a_{M^{n+}}. \quad (3)$$

If, however, deposition of the metal is accompanied by formation of an alloy on the cathode, the activity of the metal is diminished. From Eqn. (2) the equilibrium potential of the metal may be expected to be more positive under these conditions than when it is deposited on the pure metal cathode. This shift in equilibrium potential to more positive values resulting from a change in the activity of the metal in the alloy is the depolarisation $\Delta\varphi$. Its magnitude can be calculated from the well-known thermodynamic formula

$$\Delta\varphi = -\frac{\Delta\bar{G}}{nF}, \quad (4)$$

where $\Delta\bar{G}$ is the partial Gibbs free energy of the metal in

the alloy, which is directly related to the change in activity of the metal:

$$\Delta\bar{G} = RT \ln a_M. \quad (5)$$

Simultaneous solution of Eqns. (4) and (5) gives an expression for the depolarisation:

$$\Delta\varphi = -\frac{RT}{nF} \ln a_M, \quad (6)$$

from which it follows that the depolarisation must be expected to increase as the activity of the metal in the alloy decreases.

In general the activity of a metal in an alloy is determined not only by the composition of the latter but also by the nature of the interaction between the components accompanying alloy formation[110]. Hence alloys having the same proportions of the components but different types of interaction may show different amounts of depolarisation. The different cases of change in depolarisation enumerated below can be distinguished[111] in the cathodic formation of liquid alloys.

1. Ideal solutions, in which the activity of a metal is equal to its atomic fraction ($a = N$). From Eqn. (6) the magnitude of the depolarisation in this case is obviously

$$\Delta\varphi = -\frac{RT}{nF} \ln N. \quad (7)$$

Curve *1* in Fig. 1 represents calculated values for a univalent metal at 600°.

2. Solutions showing considerable negative deviations from Raoult's law. Such deviations are explained by strong interaction between the components with formation of structural clusters of intermetallic compounds in the liquid alloys. When compounds are present in alloys, the activities become less than the corresponding atomic fractions ($a_M < N_M$). In this case, as the activity of a component in the alloy decreases, the depolarisation will increase and exceed the corresponding value for an ideal solution. For example, the dependence of depolarisation on composition for the K–Pb system[112] is represented by curve *2* in Fig. 1. The most stable compound in this system is regarded as KPb with m.p. 578°.

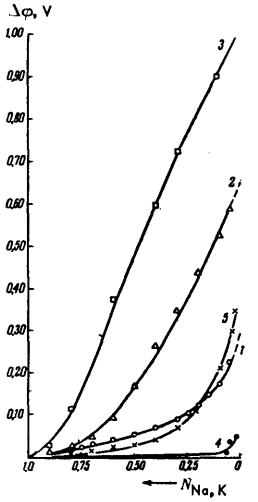


Fig. 1. Dependence of depolarisation on composition of liquid alloys:
1) ideal solution; 2) K–Pb; 3) K–Bi; 4) Na–Zn; 5) Na–Cd.

Systems in which yet more stable compounds are formed show a greater divergence of the depolarisation from the ideal value. Thus the dependence of $\Delta\varphi$ on composition for the K–Bi system[113], which forms K_3Bi (m.p. 671°) as the most stable compound, is shown by curve *3* in Fig. 1.

3. Solutions characterised by positive deviations from Raoult's law must be expected to exhibit less depolarisation than do ideal solutions. Positive deviations in activity are usually observed in alloys in which mixing of the components is accompanied by the absorption of heat, and are due to the existence of structural clusters of the pure metal. Curve *4*, representing the variation in the depolarisation of sodium in Na–Zn solution[114], lies below the curve for ideal solutions (Fig. 1).

4. Solutions characterised by positive and negative deviations from Raoult's law exhibit a complicated variation of depolarisation with composition. Such deviations in the activity of one of the components are observed when structural clusters of unsymmetrical compounds are formed[115] in the liquid solution. Examples are provided by K–Hg[116] and Na–Cd[117] solutions, the variation of $\Delta\varphi$ with composition in the latter example being plotted as curve *5* in Fig. 1.

Simultaneous discharge of the ions of two metals may also result in the formation on the cathode of an alloy in which the components are mutually insoluble and do not form compounds. In this case, the activities of both metals obviously remain unchanged, and there should be no resultant shift in the deposition potentials of the components. In the codeposition of lead and copper[118], whose mutual solubility in the solid state can be regarded as zero[119], appreciable depolarisation of the components compared with their separate deposition is not in fact observed.

For several alloys the magnitude of the depolarisation can be determined from experimental data obtained in the thermodynamic investigation of the alloys.

Methods are described in the literature[110,120] for determining the partial Gibbs function of the components of an alloy of specified composition. Tables of data usually contain integral values of the function. The latter can be converted into the partial values by one of the published methods, either by differentiation or graphically[121]. The latter procedure has been examined in detail for an alloy whose components form a continuous series of solid solutions[122,123]. The absolute value of the partial Gibbs function of each component in the alloy may considerably exceed the corresponding value of the integral function. It falls with increasing content of the given component in the alloy, while the corresponding value for the second component increases, reaching a maximum when atoms of one component are mixed with the pure second component.

Fig. 2 shows plots based on published data[124] of the variation in the partial Gibbs function of solid zinc and copper on dissolution in the solid alloys.

Alloys containing both homogeneous and heterogeneous regions show deviations from a smooth curve. In this case the relation is represented by a broken line, as in Fig. 3. Here the value of $\Delta\bar{G}$ remains unchanged in the sections representing heterogeneous systems containing two components in varying proportions.

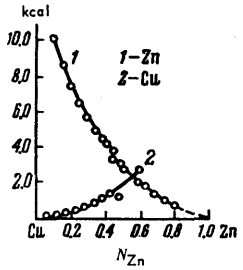


Fig.2. Dependence of partial Gibbs free energy for components on alloy composition: 1) zinc; 2) copper.

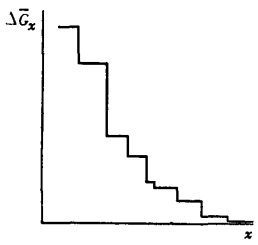


Fig.3. Variation in Gibbs free energy in alloy containing heterogeneous regions.

Thus it follows from a consideration of the thermodynamic conditions for the simultaneous electrodeposition of metals that, in all cases of alloy formation, depolarisation of each component is to be expected owing to the change in its energy state. The magnitude of the depolarisation is determined by the form of the interaction between the components in the alloy, and can be either greater or less than the theoretical value.

It must be remembered, however, that determination of the shift in the equilibrium potential caused by the change in the energy state of a metal in a solid alloy is complicated by several factors. The depolarisation can be determined directly only when liquid alloys are deposited on the cathode, where the conditions of their formation permit the practical achievement of equilibrium conditions.

IV. ELECTROCHEMICAL CONDITIONS FOR SIMULTANEOUS ELECTRODEPOSITION OF METALS

Examination of electrochemical processes has established that two metals can be deposited together on a cathode provided that they have the same deposition potential:

$$\varphi_{eq,1} - \eta_1 = \varphi_{eq,2} - \eta_2. \qquad (8)$$

It follows from Eqn. (8) that equality of the deposition potentials of two metals can be achieved by changing either equilibrium potential φ_{eq} or polarisation. Substitution of Eqn. (2) in Eqn. (8) gives

$$\varphi_{0,1} = \frac{RT}{n_1F}\ln\frac{a_{M^{n_1}+}}{a_{M_1}} - \eta_1 = \varphi_{0,2} + \frac{RT}{n_2F}\ln\frac{a_{M^{n_2}+}}{a_{M_2}} - \eta_2. \qquad (9)$$

Thus simultaneous discharge of two types of ions requires definite relations between the activities of the ions in the electrolyte, the activities of the metals in the alloy, and the overpotentials under the conditions of their codeposition. Let us examine the ways in which each of these factors can vary.

One method for equalising the deposition potentials of metals is to vary the activities of their ions in solutions of their simple salts. However, only a slight shift in the potential can be achieved in this way (a tenfold change in the activity of a univalent ion produces at room temperature a change in the equilibrium potential of 58 mV, the corresponding change for a bivalent ion being 29 mV). Therefore such a method can be used only in the codeposition of metals having similar standard electrode potentials, for example Co–Ni[125] and Sn–Pb[126].

An extremely effective method for varying the activity of ions is to incorporate them into complex ions, when both the activity of the ions in the solution and the kinetic conditions of their discharge are changed[127–130]: *i.e.* both the equilibrium potential and the polarisation are affected. By complex formation it is therefore possible not only to bring the deposition potentials of metals closer together but even to change their relative positions. This procedure is used in practice for the production of alloys whose components differ considerably in standard potential, for example Cu–Zn[29,30,33,131–134], Cu–Sn[51,52,55,56,60,135], Sn–Ni[44,61,63], Sn–Zn[53,62,65,136,137], Zn–Cd[138,139], Zn–Ni[140], Cu–Ni[47,141,142], Ag–Au[143,144], Cu–Au[145–147], Ag–Pb[37,148], etc.

Codeposition of two metals can be effected also under conditions of a limiting current of the more positive metal. In this way Zn–Cd[139] and Cu–Pb[118] alloys have been obtained from solutions of their simple salts. Investigation of the cathodic deposition of copper–lead alloys has revealed that the proportion of the current involved in the deposition of copper reaches practically the same limiting value in the presence of various additives (HNO_3, KNO_3, NH_4Cl, and $H_6C_4O_6$) at different cathode potentials. Simultaneous deposition of lead and copper takes place close to the deposition potential of pure lead, and under conditions of a limiting current of the copper. The fraction of the current due to the deposition of copper increases to values considerably exceeding the limiting current of copper in the absence of lead. This increase is explained by intensified convection of the solution near the cathode during the discharge of the heavy lead ions, as a result of which the supply of copper ions from the solution to the cathode surface is increased.

In this case the proportion of copper in the deposit is determined, for a given concentration of its ions in the solution, by the conditions governing their diffusion to the cathode surface. In conformity with the equation derived by Kheifets and Rotinyan[149], it can be assumed that

$$C_{Cu} = \frac{D[Cu^{2+}]}{i_{Pb}}, \qquad (10)$$

where C_{Cu} is the percentage of copper in the deposit and D the diffusion coefficient.

Thus under these conditions the composition of the deposit is independent of the cathode potential, and can be

controlled by varying the current density i_{Pb} involved in the deposition of lead.

It is usually supposed that the production of alloys under conditions of a limiting current of one of the components results in deposits of unsatisfactory quality. It has been shown[118] that the quality of a deposit is determined by the relative quantities of the components deposited on the cathode. Dense, finely crystalline deposits can be obtained only by the discharge of ions of the more electropositive metal into a dense mass of the other metal. In the case of copper–lead alloys, satisfactory deposits have been obtained at current efficiences of lead deposition which do not fall below 50%.

A second condition for the simultaneous deposition of metals which follows from Eqn. (9) is the presence of definite relations between the activities of the metals in the alloy. The chief aspects of this condition have been discussed in Section III, but here it must be remembered that alloy formation on a cathode can also occur by interaction between a deposited metal and the material of the cathode. In the deposition of a metal on a liquid cathode, the depolarising action of the cathode material is exhibited continuously, owing to the continual renewal of the surface by diffusion of the resulting alloy into the interior of the cathode. The magnitude of the depolarisation will then obviously be determined by the nature of the interaction accompanying alloy formation.

In practice alloy formation between a deposited metal and the cathode material is realised in the deposition of the alkali metals on a mercury cathode and in the electrolysis of molten salts with liquid metal cathodes. With a solid cathode, however, the depolarising action of the cathode material disappears owing to enrichment of the cathode surface with the deposited metal. In this case the cathode potential is low at the beginning of the process, and subsequently rises.

Finally, a third condition is variation in the overpotential under the conditions of electrodeposition of an alloy. The condition of the cathode surface during electrolysis may produce either an increase or a decrease in the overpotential. Thus during the codeposition of molybdenum and nickel an increase in the nickel overpotential has been observed[150] caused by enrichment of the alloy with molybdenum.

The temperature dependence of the overpotential can also be used to vary the conditions of the simultaneous deposition of metals. If a high overpotential of the more electronegative metal prevents simultaneous discharge of the ions at low temperatures, its decrease with rise in temperature may make electrodeposition of an alloy possible. If, however, the high overpotential characterises the more electropositive metal, a rise in temperature may shift its potential and upset the process of codeposition. However, the magnitude of the overpotential will have an appreciable effect on the displacement of the potentials of the few metals whose deposition is accompanied by considerable overpotential. With most metals, which are characterised by low overpotential, it can be expected that the overpotential will be low under conditions of simultaneous electrodeposition.

The conditions under which ions are discharged can be varied also by adding surface-active compounds to the electrolyte. Such additions are made in industrial electrodeposition to improve the quality of the metal deposit. The mechanism of their action has been examined in several papers. One of the first explanations of the effect of surface-active compounds, in particular of colloids, was given by Izgaryshev and his coworkers[151–154], who assumed it to be due to the formation of colloidal ionic complexes, discharge of which on the cathode occurred with difficulty compared with the discharge of the usual hydrated ions.

Later work showed[155–165] that the change in the structure of the deposits and the increase in polarisation of the electrode occurring in the presence of surface-active additives are due to adsorption of such substances on the cathode surface. The current can then remain constant over a wide range of potentials. Comparison of the polarisation curves with the capacitance of the electrode showed that the current increases over the potential range within which the maximum of the capacitance curve occurs: *i.e.* a low limiting current is observed only within the region where the organic compound is adsorbed[166–168].

The relation between the rates at which surface-active compounds are adsorbed and at which metals are deposited is of considerable significance in electrodeposition. Depending on this relationship, two possible types of effect of surface-active agents can be distinguished: (1) if the rate of adsorption of the surface-active compound is less than the rate of formation of a fresh metal surface, crystal nuclei can be formed only at isolated, unpassivated sites on the electrode[164,169,170]; the electrode polarisation will then vary with change in the true current density, but remain unchanged overall; (2) if, however, the rate of adsorption is sufficiently high, ions can be discharged only after they have penetrated the adsorbed layer, which requires an energy of activation whose magnitude is determined both by the nature of the ion and by that of the adsorbed layer. In the latter case the kinetics of the overall process[157–163] is governed by the stage preceding the actual discharge, which also explains the appearance of a practically constant limiting current. Deposits obtained under these conditions are distinguished by their uniformity.

The selective action of such adsorbed layers for ions of different metals is of especial interest, and governs the possibility of their codeposition with alloy formation on the cathode. Thus in the presence of gum-arabic and cresolsulphonic acid it becomes possible to deposit copper, zinc, and nickel together from a solution of their simple salts[171]. In the cathodic deposition of copper–lead and copper–tin alloys from simple salt solutions in the presence of surface-active substances, copper is deposited[172] first, and the quantity of the second metal deposited then increases with rise in the cathode potential. In this way it has proved possible to obtain finely crystalline, dense deposits containing up to 80% of tin.

Alloys of tin with bismuth[173] and antimony[64] have been obtained in the presence of added glue and crude phenol. The influence of surface-active additions on the deposition of tin–nickel alloys has also been studied[174].

Addition of surfactants to the electrolyte has been used also to obtain bright deposits of several alloys. Thus bright alloys of gold and copper, requiring no subsequent polishing, have been obtained from a cyanide electrolyte in the presence of thiourea[146].

The electrochemical conditions discussed above for bringing the deposition potentials of the components of an alloy close together cover only some of the most thoroughly investigated relations. In practice, the conditions determining the kinetics of the simultaneous discharge of ions

may differ from those occurring in separate deposition owing to changes in several factors, which will be considered in the following Sections.

V. METHODS OF INVESTIGATING AND LAWS GOVERNING THE SIMULTANEOUS DISCHARGE OF METAL AND HYDROGEN IONS

The phenomenon of the simultaneous discharge of ions is widely disseminated in electrochemical technology. Although it is undesirable in some cases (for example, the discharge of hydrogen ions or of ions of other metals in the production of a pure metal), in the deposition of alloys simultaneous discharge is the main process, investigation of which enables the physicochemical properties of alloys to be linked with their composition and the conditions under which they are obtained. Therefore examination of the polarisation accompanying, and the laws governing, the simultaneous discharge of ions is of considerable theoretical and practical interest. Theoretical investigation of these questions forms at the present time a complicated and little studied branch of electrochemistry.

Two types of ions are usually discharged at different rates at a given potential. Two cases can be distinguished depending on the relation between these rates of discharge. In case (1) the rate of discharge of one type of ions considerably exceeds that of the others. It occurs in the refining of metals, and investigation of its laws solves the problem of obtaining metals in a high degree of purity [149,175-178]. In case (2) the two types of ions are discharged at comparable rates. It can be realised either in the simultaneous deposition of two metals with formation of an alloy on the cathode, or in the deposition of one metal accompanied by appreciable hydrogen evolution.

The laws governing such simultaneous processes were investigated by Esin and his coworkers [179-185]. These workers derived an equation for the distribution of current between two types of ions undergoing simultaneous discharge, based on the hypothesis that the rate of discharge of ions is determined by the rate of electron transfer and by concentration polarisation. Tests of the equation on the simultaneous discharge of copper and zinc, nickel and hydrogen, and zinc and hydrogen showed satisfactory agreement between calculated and experimental results in all cases.

During recent years a method has been worked out for investigating the simultaneous discharge of ions which makes it possible to determine the rates of deposition of each component [125,186-192]. In order to explain its principle, we must first consider the peculiarities of such processes. In the discharge of ions of one type the electrode process is usually characterised by the relation between potential and current density at the electrode. When two or more types of ions are undergoing simultaneous discharge at a given potential, the current through the cathode is given by the sum of the partial currents, *i.e.* the currents due to discharge of the corresponding ions:

$$i_{total} = i_1 + i_2 + i_3 + \ldots \qquad (11)$$

In this case the polarisation curve is an aggregate curve representing the whole set of processes occurring at the cathode. Its displacement on passing from the deposition of pure metals to the deposition of an alloy may be governed by the simultaneous operation of several factors, and the effect may be different for each type of ions. For example, a change in the state of the cathode surface under conditions of simultaneous metal deposition and hydrogen evolution will produce a change in the hydrogen overpotential, which in turn would tend to change the proportion of the current due to hydrogen. In the codeposition of metals a change in the conditions of discharge can also produce different changes in the rate of deposition of each component. Furthermore, as already shown in Section III, the depolarisation of each metal depends on its energy state in the alloy. Therefore plotting the aggregate polarisation curve without taking into account the fraction of the current due to deposition of each component may lead to a view of the deposition of a given metal which is not always correct. It has been necessary to dwell on this question, since in several papers [13-15,25,33,62] the depolarisation of the components accompanying alloy deposition has been assessed from the displacement of the aggregate polarisation curves.

The kinetics of electrode processes involving simultaneous discharge of ions can be investigated only by comparing polarisation curves representing the dependence of the deposition rate of a given component on the cathode potential, such curves being termed partial polarisation curves. In the deposition of alloys such partial curves are plotted from analyses of deposits obtained at a given potential. Comparison of partial polarisation curves obtained for separate and simultaneous deposition of metals can give either the change in rate of deposition at a given potential or the shift in potential at a given current density. However, theoretical interpretation of partial polarisation curves is a matter of considerable difficulty, since accurate reproduction of experimental conditions is impossible for deposition of a metal in an alloy and in the pure form.

Rotinyan and Molotkova [191] have made a careful examination of the polarisation curve method in the case of the electrodeposition of Fe–Co alloys, and have shown that three methods can be used to compare polarisation curves. One consists in comparing a partial curve under conditions of simultaneous deposition with the curve for deposition of the pure metal from a solution containing an added inert electrolyte at a concentration equivalent to that of the second component to be deposited. This ensures that the ions of the test component should be at the same activity under conditions of separate and simultaneous deposition. However, the presence of the foreign ions leads to fresh difficulties. Thus addition of $MgSO_4$ produced an inflection on the polarisation curve of cobalt, obviously owing to the recharging of the electrode surface in the vicinity of the zero-charge potential. The displacement of the polarisation curve to more negative potentials is explained by the accumulation of magnesium ions in the outer part of the double layer, which screen the electrode surface and impede the discharge of cobalt ions. As a result, additional polarisation must be provided for the metal to be deposited under these conditions.

The second method of comparison involves deposition of the metals from solutions having the same total concentration of dischargeable ions. In this case the activity coefficient is maintained constant, but the activity of the dischargeable ions varies. The displacement of the polarisation curves is governed solely by the replacement of dischargeable ions of one metal by an equivalent quantity of the other.

In the third method the polarisation curves are compared at equal concentrations of ions of the deposited metal in pure and mixed electrolytes. If the variation in the activity coefficient of the dischargeable ions is slight under

these conditions, this method gives the most accurate values for the shift in the polarisation curves.

It has been shown experimentally [191] that, at relatively high concentrations of a component in a mixed electrolyte, all three methods of determining the displacement of the polarisation curves give similar results. At low concentrations of the ions to be deposited, however, the quantitative shift in the polarisation curves depends on the method of comparison. Nevertheless, the qualitative direction of the shift is the same in all these methods.

Examination of the partial polarisation curves makes it possible to establish the laws of the simultaneous discharge of ions and the nature of the polarisation for each component.

It can now be accepted as established that the deposition of many metals involves a stage of slow discharge of their ions [127,193-195]. Several investigations have also shown [125,190-192,196-200] that the character of the polarisation of each metal remains unchanged on passing to conditions of codeposition. In this case the relative rates of the simultaneous discharge of two types of ions can be expressed by an equation derived by Kheifets and Reishakhrit [186] from the slow discharge theory

$$\frac{A_1}{A_2}=\frac{i_1}{i_2}=\frac{k_1a_1}{k_2a_2}e^{\frac{U_2^0-U_1^0}{RT}+\frac{(\alpha_2n_2-\alpha_1n_1)F}{RT}\varphi}, \qquad (12)$$

where, for the two types of dischargeable ions, A represents the current efficiency expressed as a fraction, a the activity of the dischargeable ion adjacent to the cathode, U^0 the activation energy of the ions at the zero-charge potential, and i the fraction of the current involved in deposition of the given component, the remaining symbols having their usual significance.

Taking logarithms, we obtain from this equation

$$\log\frac{i_1}{i_2}=\log\frac{k_1}{k_2}+\log\frac{a_1}{a_2}+\frac{U_2^0-U_1^0}{2.3RT}+\frac{(\alpha_2n_2-\alpha_1n_1)F}{2.3RT}\varphi. \qquad (13)$$

Eqn. (13) yields particular relations between $\log i_1/i_2$ and $\log a_1/a_2$, T, and φ for constant values of the remaining quantities, for example.

$$\log\left|\frac{i_1}{i_2}\right|_{T,\frac{a_1}{a_2}}=\frac{(\alpha_2n_2-\alpha_1n_1)F}{2.3RT}\varphi+\text{const}. \qquad (14)$$

It is evident from Eqn. (14) that under the given conditions a linear relation should be observed between the potential and $\log i_1/i_2$.

In the codeposition of two metals uncomplicated by hydrogen evolution, a rise in cathode potential must be expected to be accompanied by an increase in the proportion of the more electronegative component. In fact, the composition of Co–Mo [18], Co–Ni [125], Sn–Pb [126], and Cr–Ni [201] deposits vary steadily with change in current density (or potential).

Increase in potential must also increase the current efficiency of metal deposition and decrease $\log i_H/i_M$ in the simultaneous deposition of a (bivalent) metal and evolution of hydrogen, when $\alpha_M n_M > \alpha_H n_H$. In the simultaneous deposition of zinc and evolution of hydrogen from strongly acid solutions [202,203], however, the increase in current efficiency of zinc deposition slows down at a definite potential, and the relation between $\log i_H/i_{Zn}$ and φ ceases to be linear [200].

These deviations have been explained [200] on the basis that the activities of the dischargeable ions in the cathode layer, occurring in Eqn. (13), are unknown during electrolysis, so that the ionic activities in the bulk of the solution are usually employed in calculations. However, ionic activities in the solution adjacent to the electrode are changed by the passage of the current, and may differ considerably from the activities of the corresponding ions in the rest of the solution. The activity of each type of ion in this layer is determined, on the one hand, by the rate of discharge at the cathode and, on the other, by the rate of supply of these ions from the solution to the cathode layer. The rate of discharge may then either exceed the rate of supply or lag behind it. Let us consider each of these cases.

In the simultaneous deposition of a metal and evolution of hydrogen from strongly acid solutions, when the rate of supply of hydrogen ions to the cathode exceeds their rate of discharge, the ensuing increase in acidity adjacent to the cathode must diminish the current efficiency of metal deposition. The rate of deposition of the metal must also fall in comparison with its rate of separate deposition, as a consequence of the partial replacement of metal ions by hydrogen ions in the cathode layer. In this case a decrease in the current efficiency of metal deposition and an increase in the value of $\log i_H/i_M$ must be expected, as have in fact been observed [202,203].

Considerably more complicated phenomena are observed when the rate of supply of hydrogen ions lags behind their rate of discharge. This case can occur in weakly acid solutions. According to Eqn. (13), the decrease in acidity of the cathode layer which occurs under these conditions must result in an increased efficiency of metal deposition. In addition, a rise in cathode potential will be accompanied by an increase in the difference in pH between the cathode layer and the bulk of the solution.

In the presence of salts of metals capable of forming sparingly soluble hydroxides or basic salts, the rise in pH in the cathode layer is limited by the pH at which these compounds are formed under the given conditions [204-208]. Formation of such compounds produces a sharp decrease in the activity of metal ions in the cathode layer, and this in turn leads to a diminished rate of discharge. As a result of these phenomena, the current efficiency of metal deposition must decrease, and the distribution of the partial currents due to hydrogen and the metal change.

Experimental investigation of the kinetics of the deposition of nickel [186] and of zinc [200] accompanied by hydrogen evolution has shown that under these conditions the process of metal deposition is in fact complicated by concentration phenomena. Similar phenomena can be expected also in the simultaneous deposition of two metals and evolution of hydrogen, which occur in many cases of the practical electrodeposition of alloys. Therefore the investigation of cathodic processes under these conditions is of considerable interest.

As a result of hydrogen evolution, the pH at the cathode may reach the value required for hydroxide formation by one of the metals, but which is insufficient for the second hydroxide. Then, as already shown above, the current efficiency for the first metal must be expected to diminish, whereas that for the second metal will increase until a definite potential is reached.

The above principles have been confirmed experimentally by an investigation of the electrodeposition of copper–

zinc alloys from oxalate electrolytes[199]. Figs. 4*a* and 4*b* show the dependence of the current efficiencies for zinc and copper deposition on potential under conditions of co-deposition. Whereas the efficiency of copper deposition steadily diminishes with rise in potential, that of zinc deposition increases to a definite "critical" [199] value, and it is only when such a potential is reached that the yield of zinc drops sharply. This difference in variation of current efficiency between copper and zinc is obviously due to the different pH values of hydroxide formation, 4.5 for $Cu(OH)_2$ and 5.9 for $Zn(OH)_2$.[204,205] Owing to the lower pH required, copper hydroxide is formed (though this may not be perceptible) from the very start of electrolysis. In the case of zinc the pH of hydroxide formation can be reached only with definite relative rates of zinc deposition and hydrogen evolution, *i. e.* at definite cathode potentials.

When these "critical" potentials are reached, the polarisation of zinc and copper becomes identical in character (Fig. 5). The partial polarisation curves have similar slopes in semilogarithmic coordinates. Then $\alpha_{Cu}n_{Cu} \simeq \alpha_{Zn}n_{Zn}$, and the distribution of partial currents should not be affected by change in potential in this case, as follows from Eqn. (14). The correctness of this view is confirmed by the curves in Fig. 4*c*.

It obviously follows that the composition of the alloy, too, will vary only up to the same potentials. Fig. 4*d* shows that, under conditions of the simultaneous discharge of copper, zinc, and hydrogen, the production of alloys of variable composition is possible only up to "critical" values of the potential. When these are reached, the composition

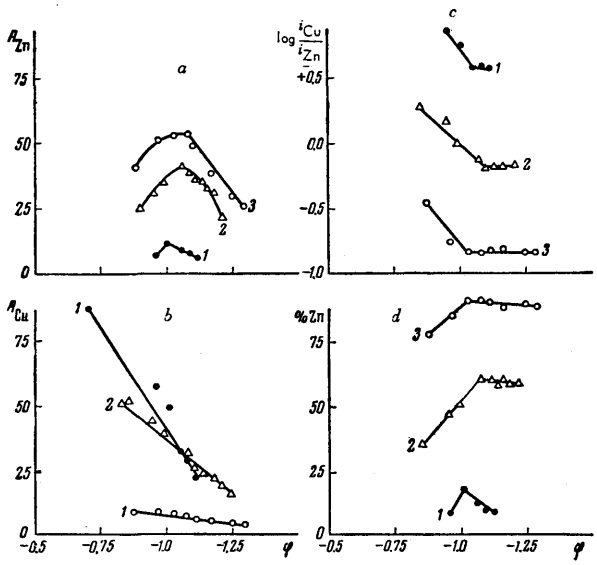


Fig.4. Dependence on cathode potential of: *a*) current efficiency of zinc deposition; *b*) current efficiency of copper deposition; *c*) distribution of partial currents; *d*) composition of copper–zinc alloy; for solutions containing (M):

	$ZnSO_4$	$CuSO_4$	$K_2C_2O_4$	H_3BO_3
1)	0.0056	0.020	0.187	0.324
2)	0.0156	0.010	0.187	0.324
3)	0.024	0.0016	0.187	0.324

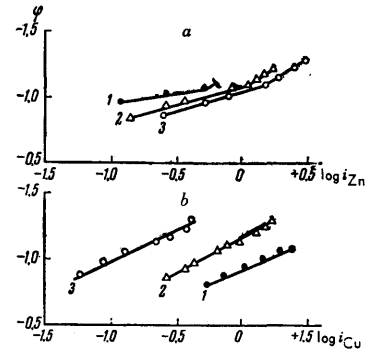


Fig.5. Partial polarisation curves obtained under conditions of codeposition of: *a*) zinc; *b*) copper. Composition of solutions as in Fig.4.

of the alloy deposits remains practically constant, except in the case of alloy No. 1, which was deposited from solutions having a very low concentration of zinc salt.

A similar type of variation in composition with change in cathode potential can be observed in the deposition of other alloys accompanied by hydrogen evolution, for example of Sn–Zn,[209] Ag–Pb,[37] Cu–Au,[146] and Cu–Zn from cyanide solutions[32,131].

From the investigation of the kinetics of metal deposition with alloy formation it can be concluded that, in both strongly and feebly acid solutions, the simultaneous evolution of hydrogen is responsible for the variation in the laws governing the simultaneous discharge of metal ions.

VI. DEPOLARISATION AND SUPERPOLARISATION OF ALLOY COMPONENTS

As shown above, alloy formation must be expected to involve depolarisation of the deposition of each component. However, comparison of partial polarisation curves by the above methods has established that, under conditions of the cathodic formation of alloys, deposition of one component may be facilitated (depolarisation) and at the same time that of the other component may be retarded (superpolarisation).

From a study of the conditions producing a shift in the potential during codeposition of metals characterised by chemical polarisation, Rotinyan and Molotkova[198] concluded that all theoretically possible cases of displacement of the partial polarisation curves — representing positive, negative, or zero depolarisation — could occur in cathodic alloy formation.

In the experimental investigation of the electrodeposition of various alloys (Co–Ni[125], Cu–Zn[131,190], Sn–Zn[209], Sn–Pb[126], Sn–Sb[64], Cu–Ni[140,210,211], Ni–Co[196], Fe–Co[198,212], Fe–Ni[197,212], Mo–Ni, and W–Ni[24]), depolarisation of the more electronegative components and superpolarisation of those deposited at the greater rate have been observed independently of the type of interaction between the components.

It has been shown above (Section III) that the phenomenon of depolarisation is determined by the thermodynamic conditions of alloy formation, *i.e.* by the change in the energy state of the metal in the alloy.

Superpolarisation of one of the components is obviously due to other factors which may appear under conditions of the simultaneous discharge of ions or the formation of a solid alloy. These factors will be considered below.

Production of a solid alloy on the cathode may be assumed to be complicated by processes associated with formation of a new type of crystal lattice. The structure of the latter is determined by the type of interaction between the alloy components[213]. Thus in the case of solid solutions the lattice of the quantitatively predominant component of the alloy is usually preserved, the atoms of the second component "taking root", as it were, in the lattice of the first, and merely changing the size of the unit cell. If the alloy contains intermetallic compounds, it forms a lattice which differs from those of the initial components. Finally, when a eutectic type of alloy crystallises, lattices may appear which are similar to those of the pure components (in the extreme ranges of composition) and resemble those of intermetallic compounds (in the regions of formation of the eutectic).

Thus, from the formation of different types of crystal lattices with different alloys, a different change in magnitude and direction of the shift in the partial curves of the components could be expected in each individual case. If it is postulated that superpolarisation (or depolarisation) of the component is caused by change in the lattice constant with variation in composition of the alloy, a definite relationship could also have been expected between them. In the deposition of Co–Fe alloys, however, the lattice constant was found to change sharply at a definite alloy composition[85], while the superpolarisation of cobalt and the depolarisation of iron vary smoothly[198].

It is clear from the above that no direct relation can be observed between superpolarisation and the type of lattice formed.

The cause of superpolarisation may be the change in the conditions of ionic discharge on passing from separate to simultaneous deposition of the components. According to Vagramyan and Fatueva[196,197,212] these conditions include change in ionic concentration adjacent to the cathode caused by the displacement of some ions by others, increased adsorption of hydrogen and the resulting hydroxides on the cathode surface, change in condition of the electrode surface (in its degree of passivation), and the consequent change in overpotential of the metals.

In actual combined systems the mutual influence of the ions undergoing discharge adjacent to the cathode leads to a breakdown in the kinetic laws established for the individual electrode reactions. In this case the condition of simultaneous discharge, Eqn. (9), can be written[180]

$$\varphi_{0.1}+\frac{RT}{nF}\ln C_1-\frac{RT}{nF}\ln\frac{\Sigma\alpha_i C_i}{\alpha_1 C_1}-\eta_1^{all}=\varphi_{0.2}+\frac{RT}{nF}\ln C_2-\frac{RT}{nF}\ln\frac{\Sigma\alpha_i C_i}{\alpha_2 C_2}-\eta_2^{all}, \quad (15)$$

where C_i is the concentration of each type of ions, and α a coefficient representing the ability of the given type of ions to penetrate the electrical double layer. The term

$$\frac{RT}{nF}\ln\frac{\Sigma\alpha_i C_i}{\alpha_1 C_1},$$

then represents the decrease in polarisation due to entry of other ions into the double layer.

On testing these assumptions in the electrodeposition of the alloys Co–Ni[196], Ni–Fe[197], and Co–Fe[212], the above workers observed an anomalous increase in the rate of reduction of the more electronegative component (Fe) accompanied by a decrease in the rate of reduction of the more electropositive component (Co or Ni). They explained the observed phenomena by the change in overpotential of metal deposition accompanying codeposition and resulting from the change in the nature of the electrode layer.

In the codeposition of nickel and cobalt the rates of reduction of both types of ions were strongly retarded[196]. Careful investigation of this phenomenon revealed that the retardation of simultaneous reactions was far greater than could have been expected solely from the change in concentration of the dischargeable ions in the double layer, and it was therefore suggested that other causes might be operating, namely a change in the state of the ions in solution and a change in the state of the electrode surface and its tendency to become passivated.

Superpolarisation of one component has been observed also in the above case of simultaneous zinc deposition and hydrogen evolution from strongly acid solutions[202,203]. As in all other cases, superpolarisation was observed with the component which separated at the greater rate, which in this system was zinc. It must be noted that here the nature of the electrode surface does not change, no hydroxides are formed, and the zero-charge potential of the zinc remains[214] unchanged.

A similar phenomenon has been observed[192] on passing from the evolution of hydrogen from a pure dilute acid to its evolution accompanied by deposition of an iron–cobalt alloy from solutions having the same pH values. The polarisation of hydrogen under these conditions is due to a slow ion-discharge step. At low temperatures, however, concentration polarisation is observed at sufficiently high current densities. The hydrogen limiting-current plateaux are then considerably lower in the presence of metal deposition than for evolution from acid.

This general presence of superpolarisation (or retardation of the rate of reduction) in the codeposition of different metals and even in simultaneous metal deposition and hydrogen evolution suggests that it has the same cause in all cases. The most probable is the mutual influence of the dischargeable ions, resulting in a change in the electrochemical conditions for their codischarge. This problem has been examined[215] for the simultaneous deposition of metals when the slow stage is the discharge of their ions.

The rate of deposition of a pure metal can be represented by the equation

$$i_M = k_M \times a_M e^{-\frac{U}{RT}} \times e^{\frac{\alpha_M nF}{RT}(\varphi_M^0-\varphi)}, \quad (16)$$

in which φ_M^0 is the zero-charge potential, and all the other symbols have the same significance as in Eqn. (12). The rate of deposition of the same metal under codischarge conditions can be expressed by a similar equation but with the subscript c attached to the symbols. Simultaneous solution of the two equations yields[215] the expression

$$\ln\frac{i_c}{i_M}=\ln\frac{k_c}{k_M}+\ln\frac{a_c}{a_M}-\frac{U_c^0-U_M^0}{RT}+\left[\frac{\alpha_c nF}{RT}(\varphi_c^0-\varphi)-\frac{\alpha_M nF}{RT}(\varphi_M^0-\varphi)\right]. \quad (17)$$

The quantity i_c/i_M represents the change in rate of deposition of the metal on passing from separate to simultaneous deposition at a given potential. Increase in the rate of deposition of the metal in the alloy ($\ln i_c/i_M > 0$) defines depolarisation, and a decrease ($\ln i_c/i_M < 0$) represents superpolarisation.

It follows from Eqn. (17) that the change in the value of $\ln i_c/i_M$ is determined primarily by the change in properties of the cathode surface when the alloy is deposited on it (if $\varphi_c^0 \neq \varphi_M^0$), by the change in activity of the dischargeable ions in the layer adjacent to the cathode, and by the change in the coefficient α_c compared with α_M.

The change in properties of the cathode surface is exhibited in particular in a shift in the zero-charge potential. No data on such potentials for different systems are available in the literature, and therefore it is not yet possible to assess sufficiently fully the way in which φ_c^0 depends on the type of interaction between the components. It is known merely that, in solid solutions [216] and amalgams [217,218], diminution in the content of the component possessing the more positive zero-charge potential produces a rapid shift in the latter to more negative values, approaching the value of φ^0 for the second component.

It follows from Eqn. (17) that a change in zero-charge potential of an alloy can have different effects on the displacement of the partial curves of each component. If the zero-charge potential of the pure metal is more negative than φ^0 for the alloy, the fourth term on the right-hand side of Eqn. (17) will, under otherwise identical conditions, become positive, resulting in depolarisation of this component. For a metal having a more positive φ^0, transition to codischarge conditions produces a change in the zero-charge potential which will cause superpolarisation.

As shown above, the change in activity of the dischargeable ions adjacent to the cathode is governed by their relative rates of discharge and of supply from the solution. Since under the conditions of simultaneous discharge of the ions of two metals their rates of supply may be very similar, the activities of the ions in the cathode layer will obviously be determined mainly by the difference in rates of discharge. If the rate of deposition of a given metal M_1 exceeds the rate of deposition of the second metal M_2, ions of the latter $M_2^{n_2+}$ will accumulate in the cathode layer during electrolysis, partly replacing the $M_1^{n_1+}$ ions. The diminished activity of these latter ions thus results in a decrease in the value of $\ln i_c/i_{M_1}$ in Eqn. (17): *i.e.* it leads to superpolarisation of M_1.

In practice it has been found that the rate of deposition of a pure metal is slowed down also by addition of inert electrolytes [191,219]. In addition to concentration phenomena, increased activation energy of discharge U^0 of the metal ions has been observed [219]. Under conditions of simultaneous discharge, the increase in U_1^0 produces an increase in absolute magnitude of $(U_c^0 - U_M^0)/RT$ in Eqn. (17), which may result in superpolarisation.

The rate of deposition of a metal must be affected in a different way by the introduction of ions having a greater rate of deposition. It is obvious that in this case the rapidly dischargeable ions cannot retard to any appreciable extent deposition of the other metal.

The change in the coefficients α on passing from separate to simultaneous metal deposition has been determined for a few alloys [125,199,215]. This shows an increase in α for each component of the alloy compared with its separate deposition, which indicates that discharge of both metal ions is facilitated by codeposition.

It follows from the above discussion that, in consideration of the laws of the codischarge of ions under conditions of alloy electrodeposition, the displacement of the polarisation curves caused by the energy of formation of the alloy must be distinguished from the displacement due to a change in the nature and state of the cathode surface and in the electrochemical conditions of deposition. Whereas the former is always in the direction of more positive potentials (depolarisation), the direction of the latter may vary depending on which kinetic factors in the discharge predominate.

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MECHANISM OF CORROSION WITH LIMITED ACCESS OF ELECTROLYTE

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1. INTRODUCTION

Many engineering structures, items of chemical equipment, and instruments corrode most strongly, strange as it may seem, at those places to which access of the corrosive medium is difficult (flanged unions, shut-off equipment, hydraulic seals, constructional gaps and crevices, etc.).

This dangerous and widespread type of corrosion, which at first was most definitely and clearly exhibited in structural gaps and crevices, was called in the literature "crevice corrosion". Nowadays this term no longer reflects the variety of corrosion phenomena which arise as a result of restricted access of electrolyte to individual parts of fabrications and equipment. However, since this term has already taken deep root in the literature, we shall preserve it in the present review, but use it in a wider sense to cover, besides corrosion in crevices, selective linear dissolution of metals at the boundary of several phases, the corrosion of structures along the water-line, the development of pitting, etc.

Crevice corrosion plays an important part in the breakdown of structures in chemical equipment, diesel engines, atomic reactors, and instruments. Intense corrosion